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(21) International Application Number: PCT/US96/14634 (22) International Filing Date: 12 September 1996 (12.09.96) (30) Priority Data: 08/548,438 26 October 1995 (26.10.95) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventors: IQBAL, Mohammed; 3M Austin Center, 6801 River Place Boulevard, Austin, TX 78726-9000 (US). PAFF, Armin, J.; 3M Austin Center, 6801 River Place Boulevard, Austin, TX 78726-9000 (US). WILLIAMS, Donald, J.; 3M Austin Center, 6801 River Place Boulevard, Austin, TX 78726-9000 (US). FAROOQ, Omar; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). TWEETEN, David, W.; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: NEAVEILL, Darla, P. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).			(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  Published With international search report.
(54) Title: COMPOSITION FOR AN INK-JET RECORDING SHEET			
(57) Abstract  A non-cross-linked composition suitable for coating onto an ink-jet recording sheet comprising: a) at least one nonionic fluorocarbon surfactant, b) at least one alkanolamine metal chelate wherein said metal is selected from the group consisting of titanium, zirconium and aluminum, and c) at least one polymer selected from the group consisting of hydroxycellulose and substituted hydroxycellulose polymers, such composition being cross-linkable when subjected to temperatures of at least about 90 °C.			

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## COMPOSITION FOR AN INK-JET RECORDING SHEET

### Field of the Invention

The invention relates to a noncrosslinked composition suitable for use as an ink-jet recording medium, and a polymeric recording sheet coated with such compositions and subsequently crosslinked, such sheet being suitable for imaging in an ink-jet printer.

### Description of the Art

Imaging devices such as ink-jet printers and pen plotters are established methods for printing various information including labels and multi-color graphics. Presentation of such information has created a demand for ink receptive imageable receptors, especially transparent receptors, that are used as overlays in technical drawings and as transparencies for overhead projection. Imaging with either the ink-jet printer or the pen plotter involves depositing ink on the surface of these transparent receptors. These imaging devices conventionally utilize inks that can remain exposed to air for long periods of time without completely drying. Since it is desirable that the surface of these receptors be dry and non-tacky to the touch soon after imaging, even after absorption of significant amounts of liquid, it is desirable that transparent materials for imaging be capable of absorbing significant amounts of liquid while maintaining some degree of durability and transparency.

Generation of an image by an ink-jet printer results in large quantities of solvent, generally blends of glycols and water, remaining in the imaged areas. Diffusion of this solvent into unimaged areas can result in "bleeding" of the image, when the dye is carried along with the solvent.

U.S. Patent 5,141,797 discloses opaque ink-jet recording sheets including a water soluble polymeric binder, a titanium chelate crosslinking agent, and an inorganic filler with a high absorption capacity, e.g., silica. The filler is present in a ratio to polymeric binder of from 2:1 to 7:1. Paper substrates are preferred. Only single layer coatings are disclosed.

Liquid-absorbent materials disclosed in U.S. Patent No. 5,134,198 disclose one method to improve drying and decrease dry time. These materials comprise

crosslinked polymeric compositions capable of forming continuous matrices for liquid absorbent semi-interpenetrating polymer networks. These networks are blends of polymers wherein at least one of the polymeric components is crosslinked after blending to form a continuous network throughout the bulk of the material, and through which the uncrosslinked polymeric components are intertwined in such a way as to form a macroscopically homogenous composition. Such compositions are useful for forming durable, ink absorbent, transparent graphical materials without the disadvantages of the materials listed above.

WO 8806532 discloses a recording transparency and an aqueous method of preparation. The transparency is coated with a hydroxyethylcellulose polymer or mixture of polymers. The coating solution may also contain a surfactant to promote leveling and adhesion to the surface, and hydrated alumina in order to impart pencil tooth to the surface.

U.S. Patent No. 5,277,965 discloses a recording medium comprising a base sheet with an ink receiving layer on one surface, and a heat absorbing layer on the other, and an anti-curl layer coated on the surface of the heat absorbing layer. The materials suitable for the ink receptive layer can include hydrophilic materials such as binary blends of polyethylene oxide with one of the following group: hydroxypropyl methyl cellulose (Methocel), hydroxyethyl cellulose; water-soluble ethylhydroxyethyl cellulose, hydroxybutylmethyl cellulose, hydroxypropyl cellulose, methyl cellulose, hydroxyethylmethyl cellulose; vinylmethyl ether/maleic acid copolymers; acrylamide/acrylic acid copolymers; salts of carboxymethylhydroxyethyl cellulose; cellulose acetate; cellulose acetate hydrogen phthalate, hydroxypropyl methyl cellulose phthalate; cellulose sulfate; PVA; PVP; vinyl alcohol/vinylacetate copolymer and so on.

U.S. Patent No. 5,068,140 discloses a transparency comprised of a supporting substrate and an anticurl coating or coatings thereunder. In one specific embodiment, the transparency comprises of an anticurl coating comprising two layers. The ink receiving layer in one embodiment is comprised of blends of poly(ethylene oxide), mixtures of poly(ethylene oxide) with cellulose such as sodium carboxymethyl cellulose, hydroxymethyl cellulose and a component selected from the group consisting of (1) vinylmethyl ether/maleic acid copolymer; (2) hydroxypropyl cellulose;

(3) acrylamide/acrylic acid copolymer, (4) sodium carboxymethylhydroxyethyl cellulose; (5) hydroxyethyl cellulose; (6) water soluble ethylhydroxyethyl cellulose; (7) cellulose sulfate; (8) poly(vinyl alcohol); (9) polyvinyl pyrrolidone; (10) poly(acrylamido 2-methyl propane sulfonic acid); (11) poly(diethylenetriamine-co-adipic acid); (12) poly(imidazoline) quaternized; (13) poly(N,N-methyl-3-S  
5 dimethylene piperidinium chloride; (14) poly(ethylene imine)epichlorohydrin modified; (15) poly(ethylene imine) ethoxylated; blends of poly( $\alpha$ -methylstyrene) with a component having a chlorinated compound.

U.S. Patent No. 4,554,181, discloses a recording sheet for ink-jet printing  
10 having a single layer coated on a substrate. The coating, which may be on paper or film substrates, contains two key components; a mordant, and a water soluble polyvalent metal salt. The mordant is a cationic polymer material, designed to react with an acid group present on a dye molecule. The water soluble polyvalent metal salt may be from a wide selection of metals, those of group II, group III, and the transition  
15 metals of the periodic table of elements. Specific salts mentioned include calcium formate, aluminum chlorohydrate, and certain zirconium salts. A two-layer system is not disclosed.

U.S. Patent No. 4,141,797, discloses ink-jet papers having crosslinked binders, and opaque sheets. The opacity is achieved by using a paper stock, and by including  
20 an inorganic filler in the coated layer. An titanium chelate cross linking agent is also disclosed. Tyzor® TE is specifically mentioned. Three other patents disclose the generic use of titanium compounds as cross-linking agents, i.e., U.S. Patent Nos. 4,609,479, 3,682,688, and 4,690,479. Binder polymers, including gelatin materials, are disclosed, as is use of a mordant.

U.S. Patent No. 4,781,985 discloses a film support having a coating thereon, such coating containing one of two possible general structures of ionic fluorocarbon surfactants. One of these two general structures is characterized by a quaternary ammonium compound having a side chain containing a sulfide linkage; the other  
25 general structure contains the element phosphorus. It is disclosed that other  
30 fluorochemical surfactants will not provide the benefits of these two structures. No two layer coating systems are disclosed.

U.S. Patent No. 5,429,860 discloses an ink/media combination, with a purpose to arrive at a superior final copy by designing the ink to match the film, and vice-versa. An external energy source is used to effect a fix step after the ink has been brought in contact with the medium. At least one multivalent metal salt, Tyzor® 131, is

5 disclosed, as are generic organic titanates.

U.S. Patent Nos. 5,045,864 and US 5,084,340, disclose a single layer image-recording elements comprising an ink receptive layer including containing 50-80 percent of a specific polyester particulate material, i.e.,

10 poly(cyclohexylenedimethylene-co-oxydiethelene isophthalate-co-sodio-sulfobenzenedicarboxylates), 15-50% vinyl pyrrolidone, and minor amounts of a short chain alkylene oxide homopolymer or copolymer, a fluorochemical surfactant and inert particles.

The present inventors have now discovered that an inkjet film comprising a single layer, or a thick absorptive underlayer, and an optically clear thin top layer  
15 containing certain nonionic surfactants and a metal chelate provides high density images which are tack-free and permanent, and which have substantially no color bleed.

#### Summary of the Invention

The invention provides a composition suitable for use on an ink-jet recording  
20 sheet, an ink-jet recording sheet having said composition coated onto at least one major surface, and an ink-jet recording sheet having a two layer coating structure.

Compositions of the invention comprise

- a) at least one nonionic fluorocarbon surfactant
- b) at least one metal chelate wherein said metal is selected from the group  
25 consisting of titanium, zirconium, and aluminum,
- c) at least one polymer selected from the group consisting of hydroxycellulose and substituted hydroxycellulose polymers,

such composition being crosslinkable when subjected to temperatures of at least about 90°C.

30 Ink-jet recording sheets of the invention comprise a substrate having two major surfaces, at least one major surface having coated thereon a composition comprising a

nonionic fluorocarbon surfactant, at least one metal chelate selected from the group consisting of titanium, zirconium and aluminum metal chelates, and at least one polymer selected from the group consisting of hydroxycellulose and substituted hydroxycellulose polymers, said composition having been crosslinked on said  
5 substrate.

Preferred ink-jet recording sheets of the invention comprise a ink-jet recording sheet comprising a two-layer imageable coating comprising:

- a) a thick absorptive bottom layer comprising at least one crosslinkable polymeric component, and
- 10 b) an optically clear, thin top layer comprising at least one nonionic fluorocarbon surfactant, and at least one metal chelate wherein said metal is selected from the group consisting of titanium, aluminum and zirconium, said top layer having been crosslinked on said substrate by heat.

Preferred two-layer coatings comprise

- 15 a) a thick absorptive bottom layer comprising
  - i) at least one crosslinkable polymeric component;
  - ii) at least one liquid-absorbent component comprising a water-absorbent polymer, and
  - iii) from 0 to 5% of a crosslinking agent
- 20 b) an optically clear, thin top layer comprising
  - i) from 0.05% to 6% of at least one nonionic fluorocarbon surfactant,
  - ii) from 14% to 94% of a hydroxycellulose or substituted hydroxycellulose polymer,
  - 25 iii) from 5% to 80% of an alkanolamine metal chelate.

The following terms have these meanings as used herein:

1. The term "semi-interpenetrating network" means an entanglement of a homocrosslinked polymer with a linear uncrosslinked polymer.
2. The term "SIPN" refers to a semi-interpenetrating network.
- 30 3. The term "mordant" means a compound which, when present in a composition, interacts with a dye to prevent diffusion through the composition.

4. The term "crosslinkable" means capable of forming covalent or strong ionic bonds with itself or with a separate agent added for this purpose.

5. The term "hydrophilic" is used to describe a material that is generally receptive to water, either in the sense that its surface is wettable by water or in the sense that the bulk of the material is able to absorb significant quantities of water. Materials that exhibit surface wettability by water have hydrophilic surfaces. Monomeric units will be referred to as hydrophilic units if they have a water-sorption capacity of at least one mole of water per mole of monomeric unit.

6. The term "hydrophobic" refers to materials which have surfaces not readily wettable by water. Monomeric units will be referred to as hydrophobic if they form water-insoluble polymers capable of absorbing only small amounts of water when polymerized by themselves.

7. The term "chelate" means a coordination compound in which a central metal ion is attached by coordinate links to two or more nonmetal ligands, which form heterocyclic rings with the metal ion being a part of each ring.

8. The term "surfactant" means a compound which reduces surface tension, thereby increasing surface wetting.

9. The term "optically clear" means that the majority of light passing through does not scatter.

20 All parts, percents and ratios herein are by weight, unless specifically stated otherwise.

#### Detailed Description of the Invention

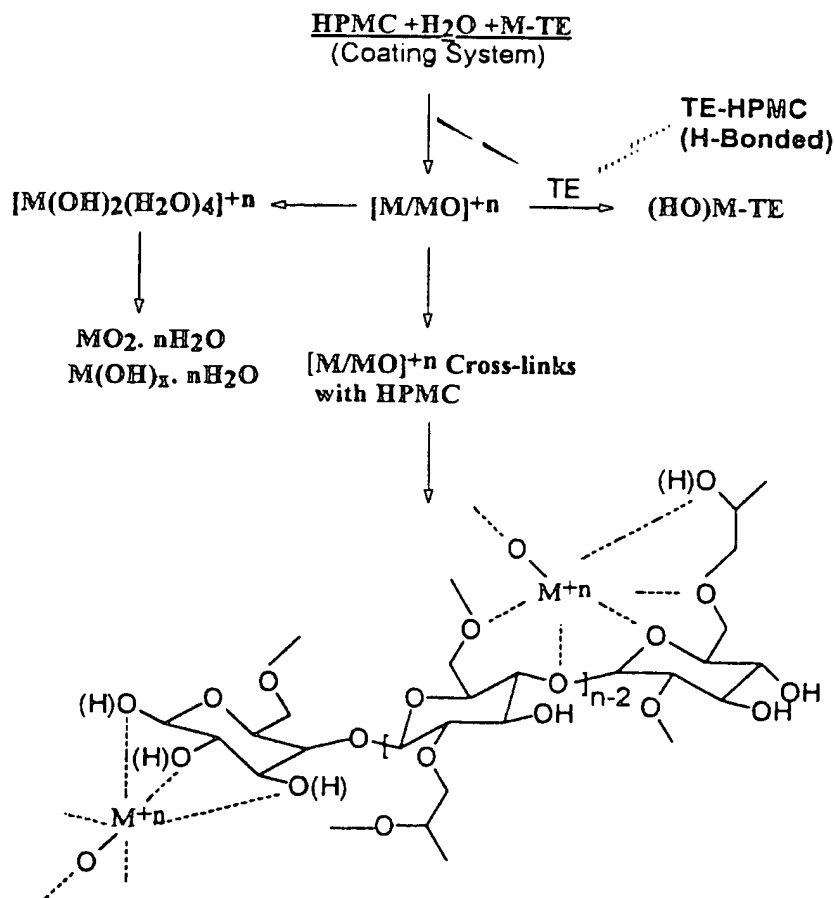
Compositions of the invention are suitable for coating onto ink-jet recording sheets. Such compositions are crosslinkable with the application of heat, and comprise at least one aluminum, zirconium, or titanium metal chelate, at least one nonionic fluorocarbon surfactant, and at least one cellulose material selected from the group consisting of hydroxycellulose and substituted hydroxycellulose polymers, such composition being crosslinkable when subjected to temperatures of at least about 90°C.

30 Useful metal chelates include titanate chelates, zirconate chelates and aluminum chelates. Such chelates typically do not undergo immediate hydrolysis when mixed



with crosslinkable materials, but will remain unreactive unless activated by raising the temperature which causes the structure of the chelate to begin breaking down. The exact temperature required will depend on the activity of the other ingredients with which the chelate is mixed, and the functional groups on the metal chelate. Useful  
5 functional groups include esters, amines, acetonates, and the like, .e.g., triethanolamine metal chelates and acetyl acetonate chelates. Chelates containing aluminum and titanate are preferred, with triethanolamine titanate chelates being highly preferred.

It is believed that the metal chelates do not undergo solvolysis when combined with the other ingredients, but rather begin to crosslink when heated during film  
10 drying. The chelates are complexed, the chelates provide titanate metal ions which are then complexed with a hydroxycellulose material, and are converted to the corresponding metal oxide or hydroxide in the cellulose matrix. The metal ions then undergo further reaction with the alkanolamine which regenerates the titanate alkanolamine chelates in hydroxylate form. The solvolysis profile is shown below:



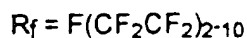
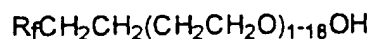
Commercially available chelates include triethanolamine titanate chelates, available as Tyzor® TE; ethyl acetoacetate titanate chelate, Tyzor® DC; lactic acid titanate chelate, Tyzor® LA and acetylacetonate titanate chelate, Tyzor® GBA, available from E.I. DuPont de Nemours (DuPont).

5        Useful nonionic fluorocarbon surfactants are those having at least a weakly hydrophilic portion and a hydrophobic portion. Useful surfactants include linear perfluorinated polyethoxylated alcohols, fluorinated alkyl polyoxyethylene alcohols, and fluorinated alkyl alkoxylates.

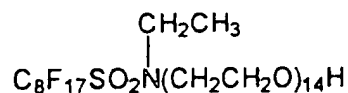
10       Preferred nonionic fluorocarbon surfactants are those having a strongly hydrophilic end and a strongly hydrophobic end. The hydrophobic end allows effective blooming to the surface of the coated layer, and the hydrophilic end provides a high

surface energy moiety on the surface which interacts with water-based inks to give uniform images. Preferred surfactants are fluorinated polyethoxylated alcohols.

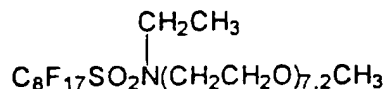
Commercially available nonionic surfactants include fluorochemical surfactants such as the perfluorinated polyethoxylated alcohols available as Zonyl FSO®, Zonyl FSN®, and the 100% pure versions thereof Zonyl FSO-100®, having the following structure,



and Zonyl FSN-100®, from DuPont; and the fluorinated alkyl polyoxyethylene alcohols available as Fluorad® FC-170C, having the following structure:



and Fluorad® 171C, available from Minnesota Mining and Manufacturing Company (3M), which can be represented as the following:



While the preferred level will vary with the particular nonionic fluorocarbon surfactant used, compositions of the invention typically comprise up to 10%, preferably from 0.05% to 6% of said surfactant. When a fluorocarbon surfactant comprising a polyethoxylated alcohol is used, the composition preferably comprises from 0.5% to 3% percent of the composition.

Ink-jet recording sheets of the inventions comprise a substrate having coated thereon a single layer which comprises the essential ingredients of compositions of the invention. Single-layer compositions of the invention must comprise at least one metal chelate wherein the metal is selected from the group consisting of zirconium, titanate and aluminum, at least one nonionic fluorocarbon surfactant, and at least one cellulose material selected from the group consisting of hydroxycellulose and substituted hydroxycellulose polymers.

The composition is not crosslinked prior to coating onto the sheet, but is coated as the uncrosslinked composition described supra, and after coating, is crosslinked by the application of heat. This is typically done in a drying oven. While not wishing to be bound by theory, it is believed that the nonionic fluorosurfactant blooms to the surface after coating. Some aging of the recording sheet is therefore preferred. This provides improved optical density properties, as well as allowing the hydrophilic portion of the surfactant to convey the large ink-drops used in ink-jet imaging through the layer where it can be absorbed. If the composition were crosslinked prior to coating, the surfactant would be trapped within the crosslinked network, requiring a much higher concentration in order for any to be present on the surface.

Preferred single-layer ink-jet recording sheets of the invention comprise from 0.5% to 6% percent of a nonionic fluorocarbon surfactant, from 5% to 80% of the metal chelate and at least one cellulosic polymer selected from the group consisting of hydroxycellulose and substituted hydroxycellulose polymers, such as hydroxyethyl cellulose, hydroxypropylmethylcellulose and the like.

Such single-layer coating may also include additional adjuvants such as mordants, polymeric microspheres, anticurling agents such as polyethylene glycols, and the like.

Preferred ink-jet recording sheets of the invention comprise a two layer coating system including an optically clear top layer, and an ink-absorptive underlayer.

The top layer is an optically clear, thin layer comprising at least one nonionic fluorocarbon surfactant, an alkanolamine metal chelate, and at least one hydroxycellulose or substituted hydroxycellulose polymer, as described, supra.

Top layers of the invention comprise from 5% to 80% of the metal chelate, preferably from 5% to 35% percent.

The top layer also comprises at least 14% to 94% of a hydroxycellulose polymer. Useful hydroxycellulosic materials include hydroxymethyl-cellulose, hydroxypropylcellulose and hydroxyethyl-cellulose and the like. Such materials are available commercially, e.g., as Methocel® series denoted A, E, F, J, K and the like, e.g., Methocel® F-50, from Dow Chemical Company.

The top layer may also include particulates, such as polymeric microspheres or beads, which may be hollow or solid, for the purpose of improving handling and flexibility. Preferred particulate materials are formed from polymeric materials such as poly(methylmethacrylate), poly(stearyl methacrylate)hexanedioldiacrylate copolymers, 5 poly(tetrafluoroethylene), polyethylene, starch and silica. Poly(methylmethacrylate) beads are most preferred. Levels of particulate are limited by the requirement that the final coating be transparent with a haze level of 15% or less, as measured according to ASTM D1003-61 (Reapproved 1979). The preferred mean particle diameter for particulate material is from 5 to 40 micrometers, with at least 25% of the particles 10 having a diameter of 15 micrometers or more. Most preferably, at least about 50% of the particulate material has a diameter of from 20 micrometers to 40 micrometers.

The absorptive underlayer comprises a polymeric ink-receptive material. Although at least one of the polymers present in the polymeric ink-receptive material is preferably crosslinkable, the system need not be crosslinked to exhibit the improved 15 longevity and reduced bleeding. Such crosslinked systems have advantages for dry time, as disclosed in U.S. Patent 5,134,198 (Iqbal).

Preferably the underlayer comprises a polymeric blend containing at least one water-absorbing, hydrophilic, polymeric material, and at least one hydrophobic polymeric material incorporating acid functional groups. Sorption capacities of 20 various monomeric units are given, for example, in D. W. Van Krevelin, with the collaboration of P. J. Hoftyzer, *Properties of Polymers: Correlations with Chemical Structure*, Elsevier Publishing Company (Amsterdam, London, New York, 1972), pages 294-296. Commercially available polymers include "Copolymer 958", a poly(vinylpyrrolidone/dimethylaminoethylmethacrylate), available from GAF 25 Corporation, and the like.

The water-absorbing hydrophilic polymeric material comprises homopolymers or copolymers of monomeric units selected from vinyl lactams, alkyl tertiary amino alkyl acrylates or methacrylates, alkyl quaternary amino alkyl acrylates or 30 methacrylates, 2-vinylpyridine and 4-vinylpyridine. Polymerization of these monomers can be conducted by free-radical techniques with conditions such as time, temperature, proportions of monomeric units, and the like, adjusted to obtain the desired properties of the final polymer.

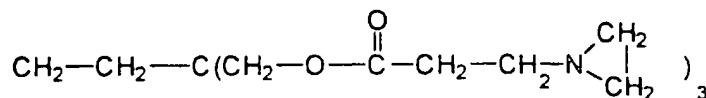
Hydrophobic polymeric materials are preferably derived from combinations of acrylic or other hydrophobic ethylenically unsaturated monomeric units copolymerized with monomeric units having acid functionality. The hydrophobic monomeric units are capable of forming water-insoluble polymers when polymerized alone, and contain no pendant alkyl groups having more than 10 carbon atoms. They also are capable of being copolymerized with at least one species of acid-functional monomeric unit.

Preferred hydrophobic monomeric units are preferably selected from certain acrylates and methacrylates, e.g., methyl(meth)acrylate, ethyl(meth)acrylate, acrylonitrile, styrene or  $\alpha$ -methylstyrene, and vinyl acetate. Preferred acid functional monomeric units for polymerization with the hydrophobic monomeric units are acrylic acid and methacrylic acid in amounts of from 2% to 20%.

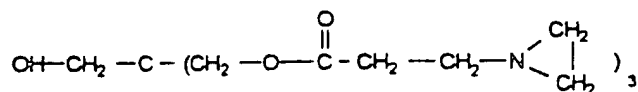
In a preferred embodiment, the underlayer coating is a semi-interpenetrating network (SIPN). The SIPN of the present invention comprises crosslinkable polymers that are either hydrophobic or hydrophilic in nature, and can be derived from the copolymerization of acrylic or other hydrophobic or hydrophilic ethylenically unsaturated monomeric units with monomers having acidic groups, or if pendant ester groups are already present in these acrylic or ethylenically unsaturated monomeric units, by hydrolysis. The SIPN for this ink-receptive coating would be formed from polymer blends comprising at least one crosslinkable polyethylene-acrylic acid copolymer, at least one hydrophilic liquid absorbent polymer, and optionally, a crosslinking agent. The SIPNs are continuous networks wherein the crosslinked polymer forms a continuous matrix, as disclosed in U.S. Patents 5,389,723, 5,241,006, 5,376,727.

Preferred SIPNs to be used for forming underlayer layers of the present invention comprise from 25 to 99 percent crosslinkable polymer, preferably from 30 to 60 percent. The liquid-absorbent component can comprise from 1 to 75 percent, preferably from 40 to 70 percent of the total SIPNs.

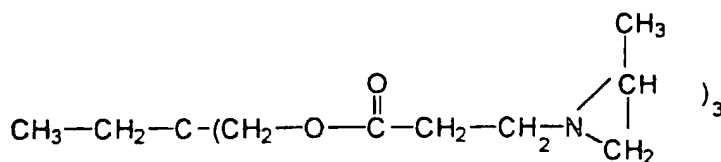
The crosslinking agent is preferably selected from the group of polyfunctional aziridines possessing at least two crosslinking sites per molecule, such as trimethylol propane-tris-( $\beta$ -(N-aziridinyl)propionate),



pentaerythritol-tris-(β-(N-aziridiny)propionate),



trimethylolpropane-tris-(β-(N-methylaziridiny) propionate)



5

and so on. When used, the crosslinking agent typically comprises from 0.5 to 6.0 percent crosslinking agent, preferably from 1.0 to 4.5 percent.

The underlayer may also comprise a mordant for reduction of ink fade and bleed. When present, the mordant preferably comprises from 1 part by weight to 20 parts by weight of the solids, preferably from 3 parts by weight to 10 parts by weight. Useful mordants include polymeric mordants having at least one guanidine functionality.

The underlayer formulation can be prepared by dissolving the components in a common solvent. Well-known methods for selecting a common solvent make use of Hansen parameters, as described in U.S. 4,935,307.

The two layers can be applied to the film substrate by any conventional coating technique, e.g., deposition from a solution or dispersion of the resins in a solvent or aqueous medium, or blend thereof, by means of such processes as Meyer bar coating, knife coating, reverse roll coating, rotogravure coating, and the like. The base layer is preferably coated to a thickness of from 0.5 μm to 10 μm, and the top layer preferably has a thickness of from 0.5 μm to 10 μm.

Drying of the layers can be effected by conventional drying techniques, e.g., by heating in a hot air oven at a temperature appropriate for the specific film substrate chosen. However, the drying temperature must be at least about 90°C, preferably at

least about 120°C in order to crosslink the metal chelate and form the colloidal gel with the hydroxycellulose polymer.

Additional additives can also be incorporated into either layer to improve processing, including thickeners such as xanthan gum, catalysts, thickeners, adhesion promoters, glycols, defoamers, antistatic materials, and the like. Likewise, additives such as the mordant, may be present in the top layer rather than the base layer or in both layers. An additive which may be present in the underlayer to control curl is a plasticizing compound. Useful compounds include, e.g., low molecular weight polyethylene glycols, polypropylene glycols, or polyethers; for example PEG 600, Pycal® 94, and Carbowax® 600.

Film substrates may be formed from any polymer capable of forming a self-supporting sheet, e.g., films of cellulose esters such as cellulose triacetate or diacetate, polystyrene, polyamides, vinyl chloride polymers and copolymers, polyolefin and polyallomer polymers and copolymers, polysulphones, polycarbonates and polyesters. Suitable polyester films may be produced from polyesters obtained by condensing one or more dicarboxylic acids or their lower alkyl diesters in which the alkyl group contains up to 6 carbon atoms, e.g., terephthalic acid, isophthalic, phthalic, 2,5-, 2, 6-, and 2,7-naphthalene dicarboxylic acid, succinic acid, sebacic acid, adipic acid, azelaic acid, with one or more glycols such as ethylene glycol, 1,3-propanediol, 1,4-butanediol, and the like.

Preferred film substrates are cellulose triacetate or cellulose diacetate, polyesters, especially poly(ethylene terephthalate), and polystyrene films. Poly(ethylene terephthalate) is most preferred. It is preferred that film substrates have a caliper ranging from 50 micrometers to 125 micrometers. Film substrates having a caliper of less than 50 micrometers are difficult to handle using conventional methods for graphic materials. Film substrates having calipers over 125 micrometers are very stiff, and present feeding difficulties in certain commercially available ink-jet printers and pen plotters.

Substrates may be opaque, transparent or translucent depending on the intended use, e.g., transmissive projection, reflective projections, or individual copies intended for brochures and the like. Where an opaque substrate is desired, the



substrate may be a film as described above, with pigmented fillers, or it may be a microvoided surface such as a paper or cloth surface.

When polyester or polystyrene film substrates are used, they are preferably biaxially oriented, and may also be heat set for dimensional stability during fusion of the image to the support. These films may be produced by any conventional method in which the film is biaxially stretched to impart molecular orientation and is dimensionally stabilized by heat setting.

To promote adhesion of the underlayer to the film substrate, it may be desirable to treat the surface of the film substrate with one or more primers, in single or multiple layers. Useful primers include those known to have a swelling effect on the film substrate polymer. Examples include halogenated phenols dissolved in organic solvents. Alternatively, the surface of the film substrate may be modified by treatment such as corona treatment or plasma treatment.

The primer layer, when used, should be relatively thin, preferably less than 2 micrometers, most preferably less than 1 micrometer, and may be coated by conventional coating methods.

Transparencies of the invention are particularly useful in the production of imaged transparencies for viewing in a transmission mode, e.g., in association with an overhead projector.

The following examples are for illustrative purposes, and do not limit the scope of the invention, which is that defined by the claims.

#### Test Methods

##### Image Density

The transmissive image density is measured by imaging the color desired, and measuring using a Macbeth TD 903 densitometer with the gold and status A filters. Black image density is evaluated by measuring the density of a solid fill black rectangle image.

##### Dry Time

The environmental conditions for this test are 70°C and 50% relative humidity (RH). The print pattern consists of solid fill columns of adjacent colors. The columns

are 0.64 cm to 1.27 cm wide, and 15-23 centimeters long. After printing the material is placed on a flat surface, then placed in contact with bond paper. A 2 kg rubber roller 6.3 cm wide is then twice rolled over the paper. The paper is then removed, and the dry time,  $D_T$  is calculated by using the following formula:

5 
$$D_T = T_D + (L_T/L_P)T_P$$

where  $T_D$  is the length of time between the end of the printing and placing the image in contact with the bond paper;  $L_T$  is the length of image transfer to paper;  $L_P$  is the length of the printed columns; and  $T_P$  is the time of printing.

#### Surface Energy

10 Surface energy values are tested using a Wilhelmy balance, model DCA-322. The testing is done at ambient room temperature, and the balance is operated at a rate of 136 microns/minute over a distance of 20 mm.

The samples are prepared by cutting two pieces of coated film, placing adhesive on the back of one piece using Scotch® Permanent Adhesive Glue Stick, and the pieces are attached together with finger pressure for several minutes in a back to back position, being careful not to touch the coated service. The samples are allowed to dry overnight before the measurements. Measurements are made using three liquids for certainty, one polar liquid (HPLC grade water), having a surface energy of 72.8 dynes/cm and one non polar liquid (99+% Pure) hexadecane, from Aldrich Chemical) 15 having a surface energy of 48.3 dynes/cm, are required; ethylene glycol (99.8%, from Aldrich Chemical) was used as the third liquid. 20

The sample is placed on a plate, and contacted with the liquid. The excess force resulting from surface tension is measured. Identical film samples are contacted with each of the liquids and the surface energy of the sample is calculated.

#### 25 Examples

##### Example 1 and Comparative Examples C2 and C3

A single layer having the following underlayer composition was coated onto a primed polyester substrate, and after being dried for 2 minutes at 100°C. The nonionic surfactant and metal chelate containing top layer described below was then coated onto

the underlayer at 75  $\mu\text{m}$  wet thickness and dried at 100°C for 1 min. This was Example 1.

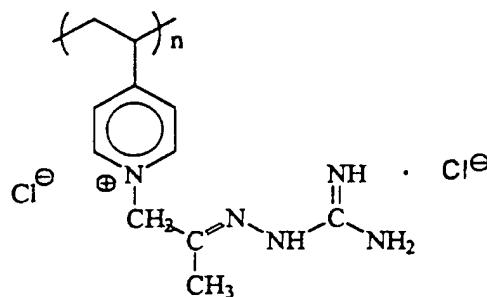
A second sample of the underlayer composition was coated, and then dried for 2 minutes at 100°C. This single layer recording sheet was Comparative Example C2.

- 5 Finally, a third sample of the underlayer composition was overcoated with a top layer containing a metal chelate of the invention, i.e., triethanolamine titanate chelate, but no nonionic surfactant, at 75  $\mu\text{m}$  wet thickness, and then dried in an oven at 120°C for 1 min. This was Example C1.

10 The ink-recording sheets were then imaged on an Epson Color *Stylus*® Printer; in two tests, Example C2 had a black density of only 0.65, Example C3 had a black density of between 0.80 and 0.84, Example 1 had a black density of between 0.90 and 0.94.

15 As can be seen, the black density of the two layer coating system with metal chelate (but no nonionic surfactant) was improved over the single layer coating which does not contain either the metal titanate chelate or nonionic surfactant; however, the two-layer coating of Example 1 containing both the nonionic surfactant and the metal ion chelate exhibited a black density which was highly improved over both comparative examples.

The mordant disclosed below has the following structure:



20 wherein n is an integer of 2 or greater.

<u>Underlayer Composition</u>		<u>Black density</u>
<u>Example C1</u>		
PVP/DMAEMA [Copolymer-958] (50%)	52%	0.65
PVA Blend [Airvol-520 + Gohsehnol KPO-6] (12.2%)	34.7%	
Polyethylene glycol [Carbowax-600](50%)	7.8%	
Mordant P134 (20%)	3.8%	
Hydroxypropylmethyl[Methocel® F-50] (4%)	1.4%	
Cross-linker XAMA-7 (16%)	0.33%	

<u>Top Layer Composition for Example 1</u>		<u>Black density</u>
HPMC (3.5%)	63%	0.94-0.90
Titania-triethanolamine-complex [Tyzor® TE] (80%)	34%	
Zonyl® FSO Surfactant (10%)	3%	

<u>Top Layer Composition for Example C2</u>		<u>Black density</u>
Hydroxypropylmethylcellulose [HPMC] (3.5%)	65%	0.84-0.80
Titania-triethanolamine-complex [Tyzor® TE] (80%)	35%	

#### Examples 3-9

These examples show the variation of black density in the film in Example 1 with the variation of Zonyl® FSO fluorochemical surfactant levels. The films were imaged in an Epson Color *Stylus®* Printer and the densities were measured by densitometer under ambient conditions.

<u>Example No.</u>	<u>Zonyl® FSO (% wt)</u>	<u>Black density</u>
3	1.0	0.95-0.90
4	1.5	0.95-0.90
5	2.0	0.95-0.88
6	2.5	0.92-0.88
7	3.0	0.92-0.88
8	4.0	0.92-0.88
9	5.0	0.92-0.88

#### Example 10

The underlayer was coated as described in Example C1, and a top layer containing a metal chelate of the invention, i.e., an aluminum triethanolamine chelate, and a nonionic surfactant was coated onto the underlayer in at 75  $\mu$ m wet thickness at 120°C for 1 min.

Example 10Black density

HPMC (3.5%)	63	
Aluminum-triethanolamine complex (84%)	35	1.04-1.01
Zonyl® FSO Fluorochemical surfactant (10%)	2%	

Examples 11-15

These examples show the variation of black density in the film of composition in example 10, with Zonyl® FSO fluorochemical surfactant levels.

<u>Example No.</u>	<u>Zonyl® FSO Surfactant (%wt)</u>	<u>Black density</u>
11	0.5	1.01
12	1	1.02-1.00
13	2	1.01-1.00
14	3	1.00-0.98
15	4	1.00-0.99

Examples 16-19

- 5        These Examples have the same composition as Example 10, except that the Zonyl® FSO was replaced with 3M fluorochemical surfactant, FC 170C. The following table shows the variation of black density when the surfactant level is varied.

<u>Films</u>	<u>FC 170C (%wt)</u>	<u>Black density</u>
16	1	0.98-0.96
17	2	0.96-0.92
18	3	0.94-0.92
19	4	0.96-0.94

Examples C20 and C21

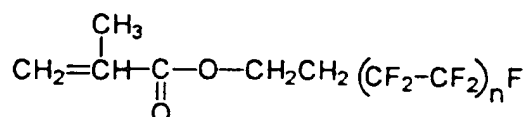
- 10       These examples show the affect of various fluorochemical surfactants used at 1%. This is a two layer system with the underlayer being identical to Example 1, except that Zonyl® FSA and Zonyl®FSJ are used as the surfactants. Both are anionic surfactants available from DuPont. Example 4, using a nonionic surfactant at 1% is provided as a comparison. As can be seen from the data, use of the anionic fluorochemical surfactants does not yield high black density values when compared to
- 15       use of the nonionic fluorocarbon surfactants.

<u>Ex. Nos.</u>	<u>Type of Surfactant</u>	<u>Surfactant wt%</u>	<u>Black Density</u>
4	Zonyl FSO-nonionic	1	0.95-0.90
C20	Zonyl FSJ-anionic	1	0.74-0.70
C21	Zonyl FSA-anionic	1	0.72-0.70

Examples 23-28

These examples show, in the composition in Example 10, the affect of various fluorochemical surfactants with different hydrophobic group on black density.

As can be seen, the anionic surfactants did not provide the increased black density. However, Zonyl® TM, a fluorocarbon methacrylate monomer having the structure



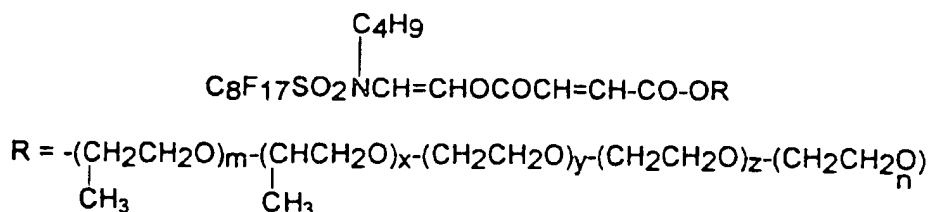
is nonionic surfactants; however, ink-recording sheets having this composition in the coating did not provide the improved black density values. It is believed that the surfactant does not contain enough hydrophilicity to draw the ink quickly into the coating, and improve the density.

<u>Ex. Nos</u>	<u>Type of Surfactant</u>	<u>Surfactant wt%</u>	<u>Black Density</u>
23	Zonyl® FSO-nonionic	1	1.02-1.00
24	Zonyl® FSA-anionic	1.5	0.80-0.78
25	Zonyl® FSA-anionic	5	0.80-0.75
26	Zonyl® TM-nonionic int.	1	0.82-0.80
27	Zonyl® TM-nonionic int.	5	0.82-0.78
28	Zonyl® 7950-anionic	5	0.84-0.81

Examples 29-31

These examples illustrate the affect of various fluorochemical surfactants which contain different hydrophilic portions on black density in the film of Example 1. These Fluorad® surfactants, available from 3M, are nonionic with the same fluorocarbon tail but different hydrophilic moieties.

Fluorad® FC-430, having the following structure:



does not provide the density improvement. This is a very large molecule with very little fluorocarbon present to balance the large polymer. It is believed that this nonionic surfactant is not hydrophobic enough to bloom to the surface of the top layer, and that such blooming is further impeded by the size of the polymer.

5

<u>Ex. Nos.</u>	<u>Type of Surfactant</u>	<u>Surfactant</u> <u>wt%</u>	<u>Black Density</u>
35	FC 170C	1	0.92-0.88
36	FC 171	1	0.94-0.90
37C	FC 430	1	0.74-0.70

Example 38 and Comparative Examples C39-C45

The underlayer in each of the following examples was machine coated onto 100  $\mu\text{m}$  polyvinylidene chloride (PVDC) primed poly(ethylene terephthalate) to give a dry coat weight of 9.7 g/m<sup>2</sup>. The coating comprises 29.6% polyvinylalcohol, available as  
10 Airvol® 523 from Air Products, 5.2% of a polyvinylalcohol having a different hydrolysis number, available as Gohensol® KP06 from Nippon Synthetic Chemical, 52.2% of a copolymer of poly(vinylpyrrolidone)/dimethylaminoethylmethacrylate, available as "Copolymer 958" from GAF, and 10% polyethylene glycol, available as Carbowax® 600 from Union Carbide.

15 The top coat for each example contained 10% Tyzor® TE, a triethanolamine titanate chelate, and 10% poly(methylmethacrylate) beads as well as the varying ingredients described in the following table for complete 100%. Each of the examples was knife coated 75  $\mu\text{m}$  thick wet atop the underlayer, and dried at about 95°C for 2 minutes. This gives a dry coating weight of 0.08-.10 g/m<sup>2</sup>.

20 The films were then evaluated by imaging a solid fill black rectangle on the Epson Stylus Printer® using the transparency print mode. The optical density of each image is then measured.

Example No.	Methocel F50 wt%	Zonyl FSO wt%	Zonyl UR wt%	Zonyl FSJ wt%	O.D.
C39	80				0.72
38	77	3			0.92
C40	79		1		0.64
C41	77		3		0.63
C42	75		5		0.62
C43	79			1	0.64
C44	77			3	0.66
C45	75			5	0.65

As can be seen from the data, the fluorocarbon of example 38, the only nonionic fluorocarbon surfactant provides superior optical density and the anionic surfactants employed in Comparative Examples C39-C45 do not.

- 5      Wilhelmy balance measurements were also completed for Example 38 and Comparative Examples C39-C45. As the following table shows, the nonionic fluorocarbon surfactant has the highest surface energy with the two anionic surfactants at all three different concentrations having much lower surface energies.

Example No.	Surfactant	Total surface energy (dynes/cm)
38	3% Zonyl FSO (3410)	38.0
C39	no surfactant	31.9
C40	1% Zonyl® FSJ	17.5
C41	3% Zonyl® FSJ	16.5
C42	5% Zonyl® FSJ	18.5
C43	1% Zonyl® UR	19.8
C44	3% Zonyl® UR	14.9
C45	5% Zonyl® UR	17.9

#### Example 46

- 10      An ink-jet recording sheet was made as follows. The substrate provided was a 100  $\mu\text{m}$  white microvoided polyester having an opacity of 90%. A two layer ink-jet coating system was coated thereon. The underlayer contained 29.6% polyvinyl alcohol as Airvol 523, 5.2% polyvinyl alcohol as Gohesol KPO6, 52.2% of a copolymer of PVP/DMAEMA as "Copolymer 958", and 10% polyethylene glycol as Carbowax®
- 15      600, and 3% of a mordant, having the structure disclosed in Example 1, supra. This layer was machine coated to give a dry coating weight of about 9.7 g/m<sup>2</sup>.



The top layer contained 77% Methocel F50, 10% Tyzor TE, 10% PMMA beads, and 3% Zonyl FSO. This layer was machine coated to give a dry coating weight of 0.81 g/m<sup>2</sup>. The ink-jet recording sheet was dried at 121°C for 1 minute.

When imaged on the Epson *Stylus*® Printer using the  
5 media setting for special coated paper, and the microweave print option, the images were of excellent quality at both 360 dpi and 720 dpi resolution.

#### Example 47

An ink-jet recording sheet was made as follows. The substrate provided was PVDC primed polyester film. A two-layer coating system was coated thereon. The  
10 underlayer contained 34% PVA blend, 52% Copolymer 958, and 7.8% Carbowax® 600, 1.4% Methocel F50, and 3.8% P134 mordant, having the structure disclosed in Example 1. This layer was machine coated to give a dry coating weight of about 9.7 g/m<sup>2</sup>.

The top layer was coated wet in 50 µm thickness, and contained 41%  
15 hydroxypropylmethyl cellulose (Methocel F50), 39% acetyl acetate (Tyzor GBA), 7.2% polyethylene glycol (Carbowax®8000), 10% poly(methylmethacrylate) (PMMA) beads, and 3% Zonyl® FSO. The ink-jet recording sheet was dried at 121°C for 1 minute.

When imaged on the Epson *Stylus*® Printer, the density was 0.92.  
20

#### Example 48

The underlayer was coated as described in Example C1, and a top layer containing 34% zirconium triethanolamine chelate, 65% hydroxypropylmethylcellulose and 1% Zonyl® FSO, was coated onto the underlayer in at 75 µm wet thickness at  
25 120°C for 1 min. The Black density was between 0.91 and 0.93.

What is claimed is:

1. A noncrosslinked composition suitable for use as an ink-jet recording medium comprising.
  - 5 a) at least one nonionic fluorocarbon surfactant selected from linear perfluorinated polyethoxylated alcohols, fluorinated alkyl polyoxyethylene alcohols, and fluorinated alkyl alkoxylates,
  - b) at least one alkanolamine metal chelate selected from the group consisting of titanate alkanolamines, titanate acetates, aluminum alkanolamines, and zirconium alkanolamines and
  - 10 c) at least one cellulosic polymer selected from the group consisting of hydroxycellulose and substituted hydroxycellulose polymers,such composition being crosslinkable when subjected to temperatures of at least 90°C.
2. A composition according to claim 1 wherein said hydroxycellulose is selected from the group consisting of hydroxypropylmethyl cellulose, and  
15 hydroxypropylethylcellulose.
3. An ink-jet recording sheet comprising a transparent substrate having two major surfaces, at least one major surface having coated thereon a composition according to claim 1 or 2, said composition having been crosslinked on said substrate by application of heat.
- 20 4. An ink-jet recording sheet comprising a two-layer imageable coating system comprising:
  - a) a thick absorptive bottom layer comprising at least one crosslinkable polymeric component, and
  - b) an optically clear, thin top layer comprising a composition according to  
25 claim 1 or 2, said top layer having been crosslinked on said substrate by application of heat.
5. An ink-jet recording sheet according to claim 4 wherein said thick absorptive bottom layer comprises

- a) at least one crosslinkable polymeric component;
- b) at least one liquid-absorbent component comprising a water-absorbent polymer, and
- c) from 0 to 5% of a crosslinking agent.

5           6.     An ink-jet recording sheet according to claim 5, wherein said liquid-absorbent component comprises a polymer selected from the group consisting of polyvinyl alcohol, copolymers of vinyl alcohol and vinyl acetate, polyvinyl formal, polyvinyl butyral, gelatin, carboxymethylcellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxyethyl starch, polyethyl oxazoline, polyethylene oxide, 10     polyethylene glycol, and polypropylene oxide.

          7.     An ink-jet recording sheet according to claim 6, wherein said polymeric liquid-absorbent component comprises polyvinyl pyrrolidone.

          8.     An ink-jet recording sheet according to claim 5, wherein said crosslinking agent is a polyfunctional aziridine selected from the group consisting of 15     tris( $\beta$ -(N-aziridiny)propionate), pentaerythritol-tris( $\beta$ -(N-aziridiny)propionate), and trimethylol propane-tris( $\beta$ -(N-methylaziridiny) propionate).

          9.     An ink-jet recording sheet according to any of claims 3-5 wherein said substrate is transparent.

          10.    An ink-jet recording sheet according to any of claims 3-5 wherein said 20     substrate is opaque.

# INTERNATIONAL SEARCH REPORT

Int. Application No.  
PCT/US 96/14634

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 B41M5/00 C08K5/00 C08K5/435

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B41M C08K C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,5 429 860 (R.P.HELD ET AL.) 4 July 1995 cited in the application see column 2, line 45 - line 68 see column 7, line 55 - column 9, line 10 see column 10, line 11 - line 27 see claims 1,3,16 ---	1-10
A	US,A,5 084 340 (W.A.LIGHT) 28 January 1992 cited in the application see column 3, line 4 - line 41 see column 6, line 65 - column 7, line 22 see claims 1,14,15; example 1 -----	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \* "A" document defining the general state of the art which is not considered to be of particular relevance
- \* "E" earlier document but published on or after the international filing date
- \* "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \* "O" document referring to an oral disclosure, use, exhibition or other means
- \* "P" document published prior to the international filing date but later than the priority date claimed

- \* "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- \* "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \* "&" document member of the same patent family

Date of the actual completion of the international search

4 November 1996

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No

PCT/US 96/14634

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5429860	04-07-95	EP-A- 0672538	20-09-95
		JP-A- 7257014	09-10-95
		US-A- 5537137	16-07-96
US-A-5084340	28-01-92	NONE	